

# CONTENTS

<b>Contributors</b>	<b>xv</b>
<b>Preface to the Second Edition</b>	<b>xvii</b>
<b>Preface to the First Edition</b>	<b>xix</b>
<b>List of Photographs</b>	<b>xxii</b>
<b>Abbreviations</b>	<b>xxiii</b>
<b>Symbols</b>	<b>xxv</b>
<b>PART I BASIC CONCEPTS</b>	<b>1</b>
<b>1. Electric Currents in Ionic Conductors</b>	<b>3</b>
1.1 Various Types of Conductors, 3	
1.2 Ions in Electrolyte Solutions, 4	
1.3 Conductivity of Electrolyte Solutions, 5	
1.4 Circuits Involving Ionic Conductors. Electrodes, 9	
1.5 Passage of Current Through Electrodes. Electrode Reactions, 10	
1.6 Classification of Electrodes and Electrode Reactions, 12	
1.7 Faraday's Laws, 15	
1.8 Equations for Mass Balance, 16	
1.9 Sign Convention for Currents and Fluxes, 18	
<b>2. Electrode Potentials</b>	<b>19</b>
2.1 Interfacial Potential Differences (Galvani Potentials), 20	
2.2 Exchange Currents, 23	
2.3 Open-Circuit Voltages, 24	
2.4 Electrode Potentials, 26	
2.5 Cell Voltage at Nonzero Current, 29	
<b>3. Thermodynamics of Electrochemical Systems</b>	<b>33</b>
3.1 Conventional and Undefined Parameters, 33	
3.2 Thermodynamic Functions in Electrochemistry, 34	

3.3	Thermodynamic Activity, 36	
3.4	Equations for the EMF of Galvanic Cells, 39	
3.5	Concentration Dependence of Electrode Potentials, 41	
3.6	Special Thermodynamic Features of Electrode Potentials, 46	
<b>4.</b>	<b>Mass Transfer in Electrolytes</b>	<b>51</b>
4.1	Basic Laws of Ionic Diffusion in Solutions, 51	
4.2	Limiting Diffusion Currents in Electrolytes, 53	
4.3	Ionic Transport by Migration and Diffusion, 55	
4.4	Convective Transport, 60	
<b>5.</b>	<b>Phase Boundaries (Interfaces) Between Miscible Electrolytes</b>	<b>69</b>
5.1	Types of Interfaces Between Electrolytes, 69	
5.2	Potentials Between Similar Electrolytes (Diffusion Potentials), 71	
5.3	Distribution of the Ions Between Dissimilar but Miscible Electrolytes, 73	
5.4	Distribution of Ions in Cells with Membrane, 75	
5.5	Galvanic Cells with Transference, 76	
<b>6.</b>	<b>Polarization of Electrodes</b>	<b>79</b>
6.1	Basic Concepts, 79	
6.2	Laws of Activation Polarization, 82	
6.3	Diffusional Concentration Polarization, 89	
6.4	Superposition of Concentration and Activation Polarization, 93	
<b>7.</b>	<b>Aqueous Electrolyte Solutions</b>	<b>99</b>
7.1	Electrolytic Dissociation, 99	
7.2	Ionic Solvation (Hydration) in Solutions, 106	
7.3	Activity of Real Electrolyte Solutions, 112	
7.4	Physical Theories of Ion-Ion Interactions, 116	
<b>8.</b>	<b>Nonaqueous Electrolytes</b>	<b>127</b>
8.1	Different Types of Electrolytes and Their Practical Utilization, 127	
8.2	Nonaqueous Electrolyte Solutions, 128	
8.3	Ionically Conducting Melts, 131	
8.4	Inorganic Solid Electrolytes, 134	

<b>9. Electron Work Functions and Volta Potentials</b>	<b>139</b>
9.1 Surface Potential of a Phase, 139	
9.2 Work Functions, 140	
9.3 Volta Potentials, 143	
9.4 Two Problems in Electrochemistry, 144	
<b>10. Structure and Properties of Surface Layers</b>	<b>147</b>
10.1 Electrical Structure of Interphases, 148	
10.2 Adsorption Phenomena, 156	
10.3 Thermodynamics of Surface Phenomena, 162	
10.4 Mercury Electrode Surface, 169	
10.5 Platinum Electrode Surface, 172	
10.6 Surfaces of Other Electrodes, 178	
<b>11. Transient Processes</b>	<b>181</b>
11.1 Evidence for Transient Conditions, 181	
11.2 Transient Diffusion to Electrodes of Large Size, 182	
11.3 Transient Diffusion to Electrodes of Finite Size, 188	
<b>12. Electrochemical Research Techniques</b>	<b>191</b>
12.1 Reference Electrodes, 192	
12.2 Voltage and Electrode Potential Measurements (Potentiometry), 195	
12.3 Steady-State Polarization Measurements, 195	
12.4 Transient (Pulse) Measurements, 199	
12.5 Impedance Measurements, 207	
<b>PART II KINETICS OF ELECTROCHEMICAL REACTIONS</b>	<b>217</b>
<b>13. Multistep Electrode Reactions</b>	<b>219</b>
13.1 Intermediate Reaction Steps, 219	
13.2 Rate-Determining Step, 220	
13.3 Two-Step Electrochemical Reactions, 222	
13.4 Complex Electrochemical Reactions, 227	
13.5 Reactions with Homogeneous Chemical Steps, 229	
13.6 Reactions with Mediators, 233	
13.7 Parallel Electrode Reactions, 235	

<b>14. Some Aspects of Electrochemical Kinetics</b>	<b>239</b>
14.1 Energy of Activation, 239	
14.2 Kinetic Influence of the Electric Double Layer, 245	
14.3 Kinetic Influence of Adsorption, 248	
14.4 Special Features of Reactions at Semiconductor Electrodes, 250	
14.5 Reactions Producing a New Phase, 252	
<b>15. Reactions at Nonconsumable Electrodes</b>	<b>261</b>
15.1 Simple Electrochemical Reactions, 261	
15.2 Hydrogen Evolution and Ionization, 263	
15.3 Reactions Involving Oxygen, 272	
15.4 Reactions Involving Chlorine and Other Halogens, 277	
15.5 Reactions Involving Organic Substances, 280	
15.6 Reactions at High Anodic Potentials, 288	
15.7 Reaction of Carbon Dioxide Reduction, 291	
15.8 Reaction of Nitrogen Reduction, 294	
<b>16. Reactions Involving Metals</b>	<b>297</b>
16.1 Reacting Metal Electrodes, 297	
16.2 Anodic Metal Dissolution, 299	
16.3 Surface-Layer Formation, 301	
16.4 Passivation of Electrodes, 305	
16.5 Cathodic Metal Deposition, 310	
16.6 Electrochemical Metal Treatments, 315	
<b>PART III APPLIED ASPECTS OF ELECTROCHEMISTRY</b>	<b>319</b>
<b>17. Industrial Electrolytic Processes</b>	<b>321</b>
17.1 Chlor-Alkali Electrolysis, 321	
17.2 Water Electrolysis, 323	
17.3 Electrometallurgy, 323	
17.4 Electroplating, 324	
<b>18. Electrochemical Reactors</b>	<b>327</b>
18.1 Design Principles, 327	
18.2 Separators, 330	
18.3 Macrokinetics of Electrochemical Processes (Systems with Distributed Parameters), 334	

18.4	Porous Electrodes, 337	
18.5	Three-Dimensional Electrodes, 342	
<b>19.</b>	<b>Batteries (Electrochemical Power Sources)</b>	<b>343</b>
19.1	Chemical Current-Producing Reactions in Batteries, 344	
19.2	Performance of Batteries, 345	
19.3	Electrochemical Systems, 349	
19.4	Primary Batteries, 350	
19.5	Storage Batteries, 353	
19.6	Lithium Batteries, 367	
<b>20.</b>	<b>Fuel Cells</b>	<b>361</b>
20.1	Introduction, 361	
20.2	Design Principles of Fuel Cells, 363	
20.3	Proton-Exchange Membrane Fuel Cells, 364	
20.4	Direct Methanol Fuel Cells, 366	
<b>21.</b>	<b>Some Electrochemical Devices</b>	<b>369</b>
21.1	Electrochemical Capacitors and Supercapacitors, 369	
21.2	Electrochemical Transducers, 375	
<b>22.</b>	<b>Corrosion of Metals</b>	<b>379</b>
22.1	Various Types of Corrosion, 380	
22.2	Mechanisms of Corrosion Processes, 381	
22.3	Corrosion Protection, 384	
<b>23.</b>	<b>Electrochemical Methods of Analysis</b>	<b>387</b>
23.1	Conductometry, 388	
23.2	Coulometry, 388	
23.3	Amperometry, 389	
23.4	Polarography, 390	
23.5	Transient Voltammetric Techniques, 394	
23.6	Potentiometry, 398	
<b>24.</b>	<b>Electrochemistry and the Environment</b>	<b>405</b>
	<i>Alexander Skundin (Sections 24.1 to 24.4) and Alvin J. Salkind (Section 24.5)</i>	
24.1	Chemical and Electrochemical Processes, 405	
24.2	Monitoring the Environment, 406	
24.3	Purification Procedures (Elimination of Pollutants), 408	

- 24.4 Medical Applications of Electrochemistry, 411
- 24.5 Electrochemical Aspects of Bone Remodeling and Fracture Repair, 413

**PART IV SELECTED TOPICS IN ELECTROCHEMISTRY** **417**

**25. Solid-State Electrochemistry** **419**

*Ulrich Stimming and Hengyong Tu (Part A)*

Part A. Solid Electrolytes, 419

- 25.1 Defects in Solids, 419
- 25.2 Solid Ion Conductors, 425
- 25.3 Solid Mixed Ionic–Electronic Conductors, 436
- 25.4 Electrochemical Reactions at Interfaces with Solid Electrolytes, 438

Part B. Solid-State Reactions, 441

- 25.5 Heterogeneous Solid-State Reactions, 441
- 25.6 Electrochemical Intercalation, 443

**26. Conductive Polymers** **449**

*Klaus Müller*

- 26.1 Active Polymers, 449
- 26.2 Polymers with Ionic Functions, 450
- 26.3 Polymers with Electronic Functions, 457

**27. Physical Methods for Investigation of Electrode Surfaces** **467**

*James McBreen*

- 27.1 Topics of Investigation, 468
- 27.2 X-Ray Methods, 470
- 27.3 Scanning Probe Methods, 484
- 27.4 Electrochemical Quartz Crystal Microbalance, 487
- 27.5 Optical Spectroscopy, 491
- 27.6 Infrared Spectroscopy, 503
- 27.7 Electrochemical NMR, 506
- 27.8 Ex Situ Methods, 507
- 27.9 The Future of Physical Methods in Electrochemistry, 516

**28. Electrocatalysis** **521**

- 28.1 Introduction, 521
- 28.2 Electrocatalysis and Adsorption Effects, 523

28.3	Metal Electrodes: Influence of the Nature of the Metal,	524
28.4	Metal Electrodes: Influence of Surface State and Structure,	530
28.5	Highly Disperse Metal Catalysts,	535
28.6	Binary and Multicomponent Metal Catalysts,	539
28.7	Nonmetallic Catalysts,	542
28.8	Stability of Electrocatalysts,	550
28.9	Other Aspects of Electrocatalysis,	551
28.10	Discussion,	552
<b>29.</b>	<b>Photoelectrochemistry</b>	<b>557</b>
29.1	Energy Levels of Electrons,	558
29.2	Electron Photoemission into Solutions,	562
29.3	Photoexcitation of Semiconductor Electrodes,	564
29.4	Photoexcitation of Reacting Species,	570
<b>30.</b>	<b>Bioelectrochemistry</b>	<b>573</b>
30.1	Transmission of the Nervous Impulse,	575
30.2	Bioenergetics,	584
30.3	Electrochemical Methods in Biology and Medicine,	589
<b>31.</b>	<b>Electrokinetic Processes</b>	<b>595</b>
31.1	Electrokinetic Potential,	597
31.2	Basic Equations of Electrokinetic Processes,	600
31.3	Practical Use of Electrokinetic Processes,	605
<b>32.</b>	<b>Interfaces Between Two Immiscible Electrolyte Solutions</b>	<b>607</b>
	<i>Zdeněk Samec</i>	
32.1	Equilibrium Galvani Potential Difference,	608
32.2	Ideally Polarizable ITIES,	612
32.3	Polarization Measurements,	612
32.4	Structure of ITIES,	614
32.5	Charge-Transfer Rate,	616
32.6	Applications,	618
<b>33.</b>	<b>Various Electrochemical Phenomena</b>	<b>621</b>
	<i>Yurij Tolmachev (Section 33.1) and Leonid Kanevsky (Section 33.2)</i>	
33.1	Electrochromism,	621
33.2	Electrochemical Noise,	626

33.3	Electrochemical Properties of High-Temperature Superconductors, 630	
33.4	Electrochemical "Cold Fusion", 632	
<b>34.</b>	<b>Main Concepts of Elementary Reaction Act Theory</b>	<b>637</b>
	<i>Alexander Kuznetsov</i>	
34.1	Outer-Sphere Electron Transfer Reactions in the Bulk Solution, 638	
34.2	Adiabatic and Nonadiabatic Reactions, 643	
34.3	Electrochemical Electron Transfer, 645	
34.4	Electrochemical Adiabaticity Parameter. Medium Dynamics vs. Static Distribution, 650	
34.5	Adiabatic Electrochemical Electron Transfer Reactions, 652	
34.6	Electric Double-Layer Effects on the Elementary Act of Electron Transfer, 653	
34.7	Bond-Breaking Electron Transfer, 655	
34.8	Reorganization Energy of the Medium and the Frequency Factor, 657	
34.9	Electrochemical Proton Transfer, 658	
<b>35.</b>	<b>Computer Simulation in Electrochemistry</b>	<b>661</b>
	<i>Ezequiel Leiva</i>	
35.1	Introduction, 661	
35.2	Molecular(Atom) Dynamics, 662	
35.3	Monte Carlo Methods, 668	
<b>36.</b>	<b>Nanoelectrochemistry</b>	<b>679</b>
	<i>Ezequiel Leiva</i>	
36.1	Introduction, 679	
36.2	Probe-Induced Electrochemical Nanostructuring of Metallic Surfaces, 680	
36.3	Defect Nanostructuring, 681	
36.4	Tip-Induced Local Metal Deposition, 684	
36.5	Localized Electrochemical Nucleation and Growth, 686	
36.6	Electronic Contact Nanostructuring, 688	
36.7	Nanostructuring by Scanning Electrochemical Microscopy, 689	
<b>37.</b>	<b>Development of Electrochemistry</b>	<b>693</b>
37.1	First Electrochemical Power Sources, 693	
37.2	Development of a Large-Scale Electrochemical Industry, 696	
37.3	Fuel Cells and Lithium Batteries, 699	

<b>Appendix A: Derivation of the Main Equation of Debye–Hückel Theory</b>	<b>701</b>
<b>Appendix B: Derivation of the Main Equation of Gouy–Chapman Theory</b>	<b>705</b>
<b>General Bibliography</b>	<b>709</b>
<b>Author Index</b>	<b>711</b>
<b>Subject Index</b>	<b>715</b>